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COMPLETE SPECIFICATION

A Method of Making Ablative, Sinterable and Sintered Shaped Structures and Structures made thereby

We, FMC CORPORATION of San José, California, United States of America, a corporation organized and existing under and by virtue of the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a method of making ablative, sinterable and sintered shaped structures and structures made thereby; more particularly the invention relates to high temperature resistant sinterable and/or sintered shaped bodies, such as films, fibres and plates, and to a method of forming such bodies. The shaped bodies may be classed as ablative structures which, during use, are transformed or converted into sintered ceramic structures.

The term "ceramic" is used herein to designate metal or other inorganic oxides which are generally classed as glass-forming oxides. The structure may comprise a single inorganic oxide, such as boron oxide, silicon dioxide or aluminium oxide, or mixtures of the oxides. The composition may also include various materials termed "intermediates" and "modifiers" in the ceramic art. The final melting or softening point of the ceramic structure will be dependent upon the specific composition and may be varied by incorporating the various modifiers or intermediates in the structure during the process of manufacture.

Conventional glass fibres, glass wool and mineral wool, as well as fused quartz filaments are formed from a molten mass and, hence, the fibres are solid. Films or plates may be formed by an extrusion process and

other structures are formed by casting techniques.

The so-called "glass fibres" and "filaments" are utilized in forming woven fabrics. However, because of the brittleness of the filaments and fibres and the high abrasion between the fibres in a yarn, it is necessary to provide special yarn finishes to reduce abrasion and special equipment is necessary in spinning and weaving operations.

The present invention provides structures formed of mixtures of a cellulosic material and a ceramic material which forms an ablative composition which is capable of retaining its shaped structure under high temperature conditions, at which the structure is transformed into a sintered ceramic structure.

According to the present invention, there is provided a method of making an ablative, sinterable structure from a cellulosic spinning solution, such method comprising adding to, and incorporating in, the cellulosic spinning solution at least one glass-forming compound, shaping the spinning solution into the structure throughout which the cellulosic material and glass-forming compound or compounds are uniformly distributed, converting the glass-forming compound or compounds to a glass-forming oxide or oxides when the glass-forming compound or compounds does or do not comprise an oxide or oxides, and removing the solvent from the structure, the amount of the said glass-forming compound or compounds added to the cellulosic spinning solution being sufficient to provide a ratio of glass-forming oxide or oxides to the cellulosic material of between 0.2:1 to 2:1.

The shaped structure may then be subjected to an elevated temperature to effect a pyrolysis of the cellulosic and other possible organic constituents, to oxidize or burn-off

the carbon and to sinter the ceramic constituents.

5 The specific method of forming the shaped structure will, of course depend upon the desired configuration of the structure. For filaments or fibres, films and plates or certain shapes which may be formed by extrusion processes, the solution will be extruded through orifices to provide the desired configuration.

10 Other structures may be formed by casting techniques. These techniques are well known and therefore the invention will be described specifically as applied to the formation of filaments.

15 The shaped structure, when subjected to elevated temperatures, will pass through various states without alteration of its physical form. The cellulosic material will first be carbonized at relatively low temperatures. If oxygen is present, the carbon then becomes oxidized and, if the temperature is sufficiently high, the remaining ceramic constituents become sintered, i.e., the finely divided or minute particles are converted into a coherent filament without an actual fusing of the particles. During these transformations or reactions, the carbonization of the cellulosic material and the burning of the carbon as well as the sintering dissipate large amounts of heat and the filament retains substantially the identical form and structure. If it is desired to form the sintered ceramic filament or other structure, it may be subjected to heat treatment in the presence of controlled amounts of oxygen at a temperature required for sintering or the structure may be subjected to successively higher temperatures required for pyrolysis, oxidation and burning of the carbon and finally sintering. For example, the filament or other structure may be subjected to a pyrolysis treatment at a temperature of from about 250° C. to about 500° C. The temperature may then be raised to a range of from about 550° C. to about 750° C. in the presence of oxygen or air to effect an oxidation and burning-off of the carbon or other remaining organic material. The temperature is then raised to from about 800° C. to about 1500° C. or higher and maintained within such range from 10 minutes to about 60 minutes during which period the glass-forming metal oxide and other ceramic constituents become sintered. The sintering temperature will obviously depend upon the specific ceramic constituents.

55 In forming the filaments or other structure, the specific cellulosic material will dictate the spinning or casting conditions and treatments to form the cellulosic material-ceramic material fibres or structure. Where viscose is used, the ceramic constituent, for example aluminium oxide, boron oxide or silicon dioxide, may be introduced in the form of colloidal size particles, but is preferably introduced as a sodium salt or in the form of

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a solution of the sodium salt. Similarly, where a cellulose ether such as, for example, an alkali-soluble, water-insoluble hydroxyethyl cellulose solution is used as the spinning solution, the ceramic constituents may be introduced in the same manner. Where organic solvent solutions of cellulose ethers or esters are used as the spinning solution, the aforementioned oxides may be introduced in colloidal sized particles but are preferably added to the spinning dope in the form of compounds such as, for example alkyl silicates, aluminates or borates soluble in the specific solvent.

70 These spinning solutions containing the dispersed or dissolved inorganic or organic silicates, aluminates or borates are then extruded through conventional spinnerets or orifices in the usual manner to form the cellulosic material filaments or other desired structural forms containing the added substances. The added substances are converted or precipitated within the filament by suitable treatment of the filaments. For example, where the added substance is sodium silicate and the spinning solution is viscose, the spinning solution is extruded into a conventional acid spinning bath to coagulate the viscose and regenerate the cellulose and simultaneously the acid reacts with the contained sodium silicate to precipitate silicic acid in an extremely finely divided and uniformly distributed form. Where an organic solvent solution of cellulose acetate, for example, is used as the base, an alkyl silicate such as, for example, tetraethyl silicate may be dissolved in the cellulose ester solution and the filaments formed by extruding the solution through conventional spinnerets in a conventional dry spinning procedure. Subsequently, the filaments are subjected to a suitable treatment with an aqueous bath containing an organic or inorganic acid which will react with the contained silicate to precipitate silicic acid in extremely finely divided form dispersed throughout the filament. A more finely divided form of particle and more uniform distribution of the particles is obtained by incorporating the ceramic constituents in the form of soluble compounds than is obtained by adding powdered ceramic constituents. Subsequently, the filaments are dried and where the silicic acid has been precipitated, it may be converted to silica or a form of a hydrate of silica by the heat treatment.

120 The resulting filaments may be used in the form of a mass or mat of fibres for thermo-insulation purposes or as a filter for high temperature gases. The filaments may be utilized in forming a knitted or woven fabric or similar uses. In use at elevated temperatures, the filaments may pass through several stages as described hereinbefore where the cellulosic constituent is first decomposed to form carbon, then the carbon is oxidized and burned-off where air is present and finally

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the ceramic constituent sintered. It has not been definitely determined whether the precipitated silicic acid is transformed into silica or whether, during the heating treatment to which the filaments are subjected, either during processes or during use, the originally precipitated silicic acid is transformed or converted to some form of hydrate of silica. In any event, the silicic acid or hydrate of silica or silica is bound together sufficiently at temperatures below the sintering temperature so that the filament or structure retains its original configuration during these heating stages. Where the temperature in use is sufficiently high, the body becomes a sintered ceramic structure. Alternatively, the filaments after drying may be converted into sintered form by subjecting them to heat treatment either in separate steps or in a single step as described hereinbefore. The filaments may be used to form a knitted or oven fabric prior to subjecting them to the necessary high temperature treatment to convert them into sintered forms.

The filaments or other structure prior to the heat treating step exhibits substantially the same physical appearance as a corresponding structure formed of the cellulosic material. The body or structure when subjected to the pyrolytic treatment will remain in the same physical configuration. However, since the organic materials have been converted to carbon, the structure will be an intense black. If the pyrolytic treatment is conducted at lower temperatures, some of the surface carbon may be removed by rubbing the structure between the fingers. By heating to temperatures of at least about 550° C. in a vacuum or an inert atmosphere, the carbon may be converted into a form which will not readily rub off between the fingers.

The sintered filaments formed as described hereinbefore, when examined by a light microscope, exhibit a structure which is substantially identical to the structure of a viscose rayon or cellulose acetate fibre, i.e., they appear under the light microscope to be solid filaments. When examined by the use of an electron microscope, however, the longitudinal surfaces exhibit a typical sintered structure, i.e., a multiplicity of minute particles bonded together at their points of contact. The cross section of the filament is of substantially the same contour as that of the filament before the cellulosic material has been removed by the heat treatment.

It is obvious that the sintering temperature as set forth above will vary depending upon the particular glass-forming and other ceramic substances added to the spinning solution. The specific temperature set forth above is applicable for the preparation of the silica fibres and it is obvious that higher temperatures will be required for the aluminium oxide fibres because of the higher melting point of the alu-

minium oxide and lower temperatures may be used for a substance such as boron oxide.

It has been found that, where a bundle or a fabric of filaments or fibres has been subjected to the pyrolysis, oxidation and sintering treatments, the filaments retain their individual identity and do not become bonded to each other during these operations. The sintered fibres and filaments exhibit an intense white colour, are highly lustrous, are acceptably flexible and highly resilient.

The properties of the sintered fibres may be altered by treating the fibres during their production or before the pyrolytic treatment with modifying salts. For example, in forming the fibres from viscose solutions, the wet gel fibres after the final after treatment or washing may be passed through an aqueous solution of a salt of a modifying agent such as, for example, a water-soluble salt of magnesium, aluminium, potassium, or boron. Where the filaments are to be used in forming a textile, the water-soluble salt may be incorporated in a conventional yarn finish applied to the wet gel filaments, the yarn finish serving the conventional purposes in weaving and knitting apparatus. As is well known, the yarn finishes generally are aqueous dispersions or emulsions of a yarn lubricant and a surfactant and these substances will be volatilized or burned off during the subsequent pyrolysis and oxidation treatments.

Filaments and fabrics prepared as described herein have, both before and after pyrolysis, oxidation and sintering, sufficient flexibility and pliability to permit their use as a dielectric covering for electric wires, as protective clothing, as thermal-insulation material and for both liquid and gaseous filters where the fluids are at high temperatures and where ordinary fibrous materials will not withstand corrosive and high temperature conditions.

In aqueous spinning systems, the glass formers, since their compounds are soluble in water and/or alkali solutions are conveniently incorporated in the spinning solution by mixing the aqueous solution of the compound and the cellulosic solution. Thus, sodium silicate, aluminate or borate may be dissolved in water or may be dissolved in sodium hydroxide a solution and the solution mixed directly with the viscose or cellulose ether solution. Alternatively, an aqueous dispersion of finely divided silica, alumina or boron oxide may be mixed with the viscose or cellulose ether solution. The mixing of the solutions may be effected during preparation of the viscose or cellulose ether solution or the dispersion of the glass former or solution of the glass former may be introduced by the conventional injection spinning technique, i.e., the dispersion or solution is injected into the stream of viscose and thoroughly mixed with the viscose or cellulose ether just prior to extrusion of the solution

through the spinneret into the spinning bath.

In an organic spinning system, such as an organic solvent solution of a cellulose ester, the glass-forming substances may be introduced into the spinning dope either as organic solvent solutions of compounds of glass-forming substances or the finely divided glass former may be dispersed in the spinning dope in a manner similar to that described in the viscose process.

Cellulose nitrate and cellulose acetate are common cellulose esters employed in spinning or forming of filaments and films, and may be used in forming the products of the present invention. Other cellulose esters, for example, the butyrate and mixed esters, for example, the acetate-butyrate and organic solvent-soluble cellulose ethers are also satisfactory. The solvent employed in forming the spinning dope will obviously be dependent upon the specific organic solvent-soluble cellulosic material. Cellulose acetate spinning dopes commonly contain from about 20% to about 30% or 35% cellulose acetate dissolved in a solvent consisting of about 94% acetone and about 6% water. An organic solvent-soluble alkyl silicate, for example, ethyl silicate, is dissolved in the cellulose ester solution or finely divided silica, for example, is dispersed in the solution. The spinning dope is then extruded through the spinneret orifices in the conventional manner either into a warm air chamber or into a liquid bath. The filaments, after collection or after being converted into a fabric, are then treated with an aqueous acidic solution, such as aqueous hydrochloric acid containing from about 2 1/2% to 5% by weight hydrochloric acid, whereby the ethyl silicate is decomposed to form silicic acid within the fire in an extremely finely divided form distributed through the individual filaments. It is obvious that, where the finely divided silica has been dispersed in the spinning dope, it is not necessary to after-treat the filaments. The filaments or fabrics may be subjected to pyrolysis, oxidation and sintering operations, or to use as described in connection with the viscose process.

Cellulose nitrate may be utilized in the same manner. However, the solvent for the nitrate spinning dope would be methyl alcohol and ether.

Organic solvent-soluble cellulose ethers may be used as the cellulose base material in like manner. For example, methyl cellulose, ethyl cellulose or benzyl cellulose having a degree of substitution of about 0.5 to about 2.5 may be dissolved in dioxane, tetrahydrofuran or dimethylsulphoxide to form the spinning dope in which the glass former is dissolved or dispersed as described hereinbefore. After spinning and removal of the solvent, the filaments are subjected to a suitable acid treatment to precipitate the silicic acid where an organic solvent-soluble silicate was dis-

solved in the spinning dope. Filaments formed in this manner are then subjected to use or to the required pyrolysis, oxidation and sintering operations to form sintered filaments.

The amount of the glass former added to the spinning solution or dope may vary over an appreciable range. The porosity of the filaments and other properties may thereby be regulated and will vary inversely with the proportion of glass former with respect to the cellulosic material assuming the heating treatments are constant. Preferably, the glass former is incorporated in the spinning solution or dope as a soluble compound which is subsequently decomposed or converted into the glass former because, by precipitating the glass former in situ, it is more uniformly distributed throughout the filament and it is a more finely divided state, possibly in a molecularly dispersed state, than the particles which are formed by grinding and dispersing solid particles in the spinning solution or spinning dope.

The following example illustrates the forming of filaments by the viscose process which is most convenient because many of the common glass formers are soluble in alkali solutions and, hence, are soluble in the viscose spinning solutions. The preferred viscose compositions and techniques are those common for the production of high tenacity rayon of the type commonly produced for tyre cord purposes. The viscose preferably contains a modifying agent and the spinning bath preferably contains a surfactant as conventionally used in the production of conventional types of rayon. Ordinary commercial or technical grades of sodium silicate, sodium aluminate or sodium borate may be dissolved in the viscose in amounts to provide a metal oxide to cellulose ratio of from 0.2:1 up to 2:1. Merely to illustrate the invention, it may be described specifically by reference to the use of a technical grade of sodium silicate having a $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:3.25.

EXAMPLE

Viscose was prepared in a conventional manner containing 7.5% cellulose, 6.5% caustic soda and 38% carbon disulfide, based on the weight of the cellulose. During the mixing operation, 3.3% dimethylamine and 1.7% of a polyoxyethylene glycol ether of phenol containing an average of 15 ethylene oxide units per mole of phenol was incorporated in the viscose. A technical grade sodium silicate as described was added to the viscose to provide equal weights of silica and cellulose. The viscose was then allowed to ripen for about 24 hours at 18° C.

The viscose having a salt test of about 9 was then extruded through a spinneret to form a 1650 denier, 1500 filament yarn at the rate of about 40 meters per minute. The

coagulating and regenerating bath contained by weight 6.5% sulphuric acid, 14% anhydrous sodium sulphate and 4% anhydrous zinc sulphate and was maintained at a temperature of about 60° C. After an immersion length of 16 inches, the filaments were withdrawn from the spinning bath and passed over thread-advancing reels. During the passage of the filaments around the thread-advancing reels, they were stretched about 75% while being treated with a hot dilute acid solution containing about 3% by weight sulphuric acid and were then washed with water at a temperature of about 70° C. The wet gel filaments were then treated with a yarn finishing bath consisting of an emulsion of about 1.5% mineral oil, 0.8% Silicone Oil L-45 in water containing by weight about 0.25% of a surfactant, 0.5% gelatin, 10% anhydrous magnesium sulphate, 2% anhydrous aluminium sulphate and 0.5% anhydrous potassium sulphate. The filaments were then passed over drying rolls and collected on a tube.

Some samples of filaments prepared in this manner were woven into a flat fabric. Other samples were woven into a tubular fabric. Tubular fabrics, placed over ceramic cores to provide a slight tension in the fabric, a mass of loose filaments and flat fabrics were all then subjected to heat treatment. It was desired to produce sintered structures so that the heat treatment was conducted in a muffle furnace at a temperature of about 900° C. and the samples were maintained at this temperature for 30 minutes. Upon removal of the products from the furnace and cooling to room temperature, the filaments exhibited a surprising whiteness, lustre, resilience and flexibility. The filaments and fabrics, while having a somewhat harsh feel, were extremely flexible and pliable. The filaments retained their individual identities and were not cemented or adhered together.

Under the light microscope, the dried filaments prior to heat treatment exhibited a typical kidney-bean shaped cross section and a smooth, non-crenulated exterior surface. After pyrolysis, oxidation and sintering, the filaments exhibited substantially the same cross sectional and longitudinal appearance under the light microscope. When examined by means of the electron microscope at a magnification of about 100,000, the longitudinal appearance is that typical of a sintered body. The cross section illustrates a typical porous sintered structure. The individual particles appeared to be within the range of about 100Å to about 1000Å units in size.

Filaments having like structures and characteristics have been formed with the cellulose spinning solutions wherein the silica to cellulose ratio varied within the range as hereinbefore set forth. When filaments are formed as described in the specific example by the omission of the zinc sulphate from the spinning

bath, the filaments during the heat treating steps appear to be somewhat weaker in strength and cannot be satisfactorily subjected to the heat treating step while under tension. However, when such filaments are subjected to the heat treatments in relaxed condition, the final sintered filaments appear to have about the same properties as those formed when zinc sulfate is present in the spinning bath.

Sintered filaments having diameters of about 3.5 microns have been formed by the method as described.

For the production of ablative structures, a further increase in resistance to high temperature conditions is obtained by incorporating in the cellulosic matrix a high temperature resistant synthetic resin, such as epoxy resins, phenolic resins and urea-formaldehyde resins, which are well known in the art. Generally, the resins may be incorporated in the spinning solutions by conventional injection spinning methods or by impregnating the shaped article during processing with a solution or dispersion of the resin. The resin is preferably in the precondensate form and polymerizes and becomes a thermoset resinous material during processing of the filaments.

The presence of this class of resinous material distributed throughout the structure improves the strength of the ablative structures and provides another organic constituent which will dissipate considerable energy when it decomposes at high temperatures. Where it is desired to form a sintered ceramic body, the resins obviously would not be employed because, in the absence of the resins, the structures have sufficient strength to permit the necessary heat treatments. In such case, the incorporation of the resin would merely add to the cost of production without imparting any appreciable benefits.

As pointed out hereinabove, it is not known with certainty in which precise form or combination the glass-forming compounds occur in the dried and heat treated products. It would appear that in the manufacture of the products, the glass-forming oxides are probably first present as acids, for example, in the case of incorporating an alkali metal silicate in a viscose solution, silicic acid is first formed during treatment of the shaped body or structure in the acid bath. Upon drying of the product, water is removed. However, it is believed that the temperatures are not sufficiently high to remove all water and, hence, the silicon is present probably in the form of a hydrate of silica. It is believed that it is this form which imparts sufficient strength to the bodies by a bonding or possible polymerization between the particles so that the shaped article retains its shape and form when the organic material is carbonized and burned-off.

Similarly, the mechanism and action in

forming like products by introducing the glass-forming compounds in the form of finely divided powders may follow somewhat the same pattern, at least in the aqueous systems.

- 5 For example, when the very finely divided silica is incorporated in a viscose solution, it is possible that at least the surface portions of the particles become hydrated sufficiently to form a hydrate of silica or possibly silicic acid during spinning of the viscose into the acid bath. In the subsequent treatment, the hydrate of silica is sufficient to bond together the particles so that the shaped structure retains its shape and form during the subsequent heat treatment.

WHAT WE CLAIM IS:—

1. A method of making an ablative sinterable structure from a cellulosic spinning solution, such method comprising adding to, and incorporating in, the cellulosic spinning solution at least one glass-forming compound, shaping the spinning solution into the structure throughout which the cellulosic material and glass-forming compound or compounds are uniformly distributed, converting the glass-forming compound or compounds to a glass-forming oxide or oxides when the glass forming compound or compounds does or do not comprise an oxide or oxides, and removing the solvent from the structure, the amount of the said glass-forming compound or compounds added to the cellulosic spinning solution being sufficient to provide a ratio of glass-forming oxide or oxides to the cellulosic material of between 0.2:1 to 2:1.

2. A method according to claim 1, wherein a high temperature resistant resin is incorporated in the said cellulosic spinning solution and is uniformly distributed throughout the structure.

3. A method according to claim 1, wherein the structure is impregnated with a high temperature resin so that the latter is uniformly distributed therethrough.

4. A method according to claim 1, 2 or

3, wherein the cellulosic spinning solution comprises viscose and wherein the spinning solution is shaped in an acid bath.

5. A method according to claim 4, wherein the viscose is shaped by extrusion through orifices to form filaments.

6. A method according to any one of the preceding claims, wherein the glass-forming compound is sodium silicate.

7. A method according to any one of the preceding claims, wherein the structure is subjected to elevated temperatures to decompose and carbonise the cellulosic material.

8. A method of forming a sintered to shape structure, such method comprising subjecting a structure prepared by the method of any one of claims 1 to 6, to elevated temperatures to carbonise and oxidise the cellulosic material and sinter the shaped structure.

9. A method of making an ablative structure from viscose substantially as hereinbefore described with reference to the Example.

10. A method of making a sintered to shape structure substantially as hereinbefore described with reference to the Example.

11. An ablative, sinterable structure when prepared by the method of any one of claims 1 to 7 and 9.

12. A sintered to shape structure when prepared by the method of claim 8 or 10.

13. A fabric formed of filaments made by the method of any one of claims 1 to 10.

14. A fabric formed of filaments made by the method of any one of claims 1 to 7 and 9, and subsequently heated to produce a sintered structure.

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